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A modified Pariser—Parr—Pople approach to thioacetamide and thiourea

V. C. JYOTHI BHASU, ARABINDA RAY AND C. C. PATEL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012

The electronic spectra of thioacetamide (TAM) and thiourea (TU) have been reinvestigated employing variable-electronegativity Pariser-Parr-Pople (P P P) molecular orbital method. The conventional P P P- calculation has also been made for comparison. The assignment of the various transitions are discussed. A new expression, similar to Cusachs has been tried for the calculation of resonance integrals (β).

1. INTRODUCTION

Thioacetamide (TAM) and thiourea (TU) have been the subject of various electronic spectral studies (1, 2, 3). The electronic spectra of these simple thioamides were explained by Hosoya *et al* (1960) invoking the concept of intramolecular charge-transfer, where the amino (NH_2) and thiocarbonyl (C=S) groups are the electron donor and acceptor respectively. Their computed electronic transition energies, however, were not in good agreement with the experimental values. One of the reasons for this may be that these authors had arbitarily assumed some values for β_{CS} and β_{CN} . A recent CNDO calculation (Barret & Daghaidy 1975) proposed somewhat different assignment of the transitions in TAM and TU.

It was therefore, thought appropriate to recalculate the energies of electronic transitions for these molecules employing molecular orbital methods, different from those of the previous workers (Hosoya et al 1960, Barrot & Daghaidy 1975, Janseen and Sandstrom 1964). In the present study, we have made use of the variable-electronegativity P P P method (Brown & Hefferman 1958), where the valence orbital ionisation energies, one centre electron repulsion integrals and resonance integrals are derived from the variable effective nuclear charges, either directly or indirectly. The variable effective nuclear charge takes into account the shift of the π^- electron cloud within the molecule. In addition, conventional P P P-calculation, using β as an adjustable parameter against the observed electronic transitions, is also performed.

2. Method of Calculation

Carbon, nitrogen and sulfur are assumed to form the conjugated system, each nitrogen atom contributing two electrons to the conjugation.

The Fock matrix elements in the P P P approximation (Pariser & Parr 1953, Pople 1953) are given by,

$$F_{\mu\mu} = U_{\mu} + \tfrac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\nu \neq \mu} (P_{\nu\nu} - Z_{\nu}) \gamma_{\mu\nu} \qquad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \qquad (2)$$

where U_{μ} is the appropriate valence orbital ionisation energy (VOIE), $\gamma_{\mu\mu}$ the corresponding one centre two electron repulsion integral and Z_{μ} the core charge.

In the variable electronegativity approach the effective nuclear charges (Z_{eff}) of the atoms are calculated first. This is related to the atomic number, σ electrons contributed to the core and the π^- electron charge on it (Brown & Heffernan 1958, Harada 1964). The VOIE's and on centre two electron repulsion integrals are connected to the variable Z_{eff} through the following expressions,

$$U_{\mu} = A Z^2_{\text{eff}} + B Z_{\text{eff}} + C \qquad (3)$$

$$\gamma_{\mu\mu} = P Z^2_{\text{eff}} + Q Z_{\text{eff}} + R . \qquad (4)$$

The values of the coefficients are given in Table 1. A different expression (Nishimoto 1967)

Table 1 Coefficients used in the VOIE AND $\gamma_{\mu\mu}$ expressions (eqs. (3), (4))

atom	A	B	C	P	Q	R
C*	−3.527	8.96	−3.36	−0.195	7.223	−10.573
N*	−3.527	8.96	−3.36	−0.195	7.223	−10.573
S**	−0.856	−2.364	25.841	—	—	—

* taken from Harada (1964).

** Calculated by the present authors.

$$0.160\ \gamma^2_{ii} - 0.288\ \gamma_{ii} + U_i = 0 \qquad (5)$$

was employed to calculate γ_{ii} for sulfur.

For the resonance integrals we propose the following semi-emperical relation.

$$\beta_{ij} = \frac{(K - S_{ij})\ (U_i + U_j)}{4(q_i + q_j - 1)} S_{ij} \qquad (6)$$

where q_i is the π- charge on the ith centre, S_{ij} the overlap and K is a constant

The approximation suggested by Nishimoto & Mataga (1957) hah been used for the two centre two electron repulsion integral, as this has been found satisfactory for explaining the electronic transitions.

The following structural parameters are employed: bond distances: C-N = 1.325 and C = S = 1.713, all bond angles 120°. The required overlap integrals are calculated using the formulae of Mulliken *et al* (1949). Slater type atomic orbitals with the exponents modified by Burns (1964) are employed.

For the conventional P P P-calculation of TAM and TU, the VOIE and one centre electron repulsion integrals are taken from the literature (1968). The two centre repulsion integrals are calculated as mentioned above.

The initial Fock matrix is constructed from a simple Huckel type calculation. The secular equation is solved in the usual way and iteration continued until self consistency in the bond order matrix is obtained.

All computations were done in an IBM/360 Computer at the Indian Institute of Science, Bangalore.

3. Results and Discussion

The energy levels and wave functions of TAM and TU are summarised in Table 2. Furthermore the singlet-singlet transitional energies and corresponding oscillator strength are presented in Table 3.

The results obtained by the variable electronegativity and conventional P P P-methods are not very much different from each other. In the variable electronegativity P P P-method, the constant K (eq. 6) has been given values 1.05 and 1.5 for TAM and TU respectively. The final β values after itera-

Table 2. Energy levels and wave functions of TAM and TU

Compound	Variable Electronegativity P P P					Conventional P P P				
	Energy levels (eV)	Wave functions				Energy levels (eV)	Wave functions			
		S	C	N			S	C	N	
TAM	-3.104 (E_1)	0.655	-0.739	0.159		-2.926 (E_1)	0.582	-0.788	0.199	
	-9.845 (E_2)	0.742	0.587	0.324		-9.892 (E_2)	0.806	0.528	-0.266	
	-13.770 (E_3)	0.146	0.330	0.933		-13.539 (E_3)	0.104	0.315	0.943	
		N_1	N_2	C	S		N_1	N_2	C	S
TU	-1.964 (E'_1)	0.1980	0.198	-0.738	0.614	-2.018 (E'_1)	0.214	0.214	-0.777	0.553
	-9.095 (E'_2)	-0.298	-0.298	0.480	0.769	-9.707 (E'_2)	-0.260	-0.260	0.440	0.819
	-13.290 (E'_3)	-0.707	0.707	—	—	-13.104 (E'_3)	-0.707	0.707	—	—
	-15.8437 (E'_4)	0.609	0.609	0.475	0.177	-14.470 (E'_4)	0.622	0.622	0.451	0.152

Table 3. Transition energies and oscillator strength

Compound	Observed		Hosoya		Variable electronegativity		Conventional P P P	
	Transitions (nm)	oscillator strength	Transitions (nm)	oscillator strength	Transitions (nm)	oscillator strength	Transitions (nm)	oscillator strength
TAM	260.0	0.175	260.0	0.515	265 0 ($E_2 \rightarrow E_1$)	0.888	260.0 ($E_2 \rightarrow E_1$)	0.863
	211.0	0.086	167.0	0 198	205 0 ($E_3 \rightarrow E_1$)	0.062	209.0 ($E_3 \rightarrow E_1$)	0.870
TU	238.0	0.325	212.0	0.600	257 0 ($E'_2 \rightarrow E'_1$)	0.983	237.0 ($E'_2 \rightarrow E'$)	0.972
	199.0	0.234	225.0	0.529	286.0 ($E'_3 \rightarrow E'_1$)	0.204	195.0 ($E'_3 \rightarrow E'_1$)	0.234
			136.0	0.025	130.0 ($E'_4 \rightarrow E'_1$)		157.0 ($E'_4 \rightarrow E'_1$)	

tion to self consistency in the bond-order matrix are $\beta_{CS} = -1.21$eV and $\beta_{CN} = -1.28$eV in TAM and $\beta_{CS} = -1.71$ eV and $\beta_{CN} = -2.10$ eV. in TU. In the conventional P P P-method, the values used are $\beta_{CS} = -1.20$eV and $\beta_{CN} = -1.22$eV in the case of TAM and $\beta_{CS} = -1.58$eV and $\beta_{CN} = -1.62$eV in TU.

The highly intense bands of TAM at 210 nm and 260 nm were assigned by Hosoya *et al* 1960) in the following way. Their calculation attributed the 260 nm absorption peak to the electronic transition from ground state to the first exsited state having more or less equal contribution ($\sim$42%) from locally excited and charge transfer configurations. A recent calculation by Barrett *et al* (1975) supports the previous assignment. In the present study this intense band at 260 nm is assigned to $\pi_{C=S} \longrightarrow \pi^*_{C=S}$ transition. The 210 nm band of TAM was assigned by Hosoya *et al* to the transition from the ground state to one consisting of $\sim$55% locally excited and $\sim$40% charge transfer configuration. Barrett et al, however, assigns this band to a $^1n_S \longrightarrow {}^1\pi^*$ transition. In the present investigation, the 210 nm band is attributed to the transition from an orbital consisting mainly of a nitrogen π-orbital to an antibonding π C = S orbital. This band can therefore be assigned to a $1\pi_N \longrightarrow 1\pi^*_{C=S}$ transition. The assignment of the band to $1_{nS} \longrightarrow 1\ \pi^*$ transition from CNDO calculation, is not favoured by the present authors.

The 236 nm band in thiourea was assigned to a transition from the ground state to an excited state comprising ($\sim$53%) locally excited and ($\sim$20%) charge transfer configurations (1). The main contribution in otherwords, was the $\pi_{C=S} \longrightarrow \pi^*_{C=S}$ transition. This assignment is supported even in the present study. This band of TU is comparable to the 260 nm band of TAM.

Hosoya *et al* attributed the 197 nm band to a charge transfer transition in thiourea. The CNDO calculation favoured $1_{nS} \longrightarrow 1_{\pi}{}^*$ transition for this absorption. We prefer to assign this band to a $^1\pi_N \longrightarrow {}^1\pi^*_{C=S}$ transition, similar to the 210 nm band of TAM.

The results of the present investigation are more or less compatible with those of Hosoya *et al*. Some of the assignments propounded by Barrett are difficult to accept as explained in the preceeding discussion. It is well known that CNDO method is not well suited for interpreting the electronic transitions of a conjugate system.

The number of empirical parameters is reduced in the present modified variable electronegativity method. This approach is more realistic than the conventional P P P method. Once the empiricism in the factor K is disposed

of, this method it is hoped, will be of much help for the P P P-calculation of polar molecules.

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